



GB04/1680



INVESTOR IN PEOPLE

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales

NP10 800	
REC'D 28 MAY 2004	
WIPO	PCT

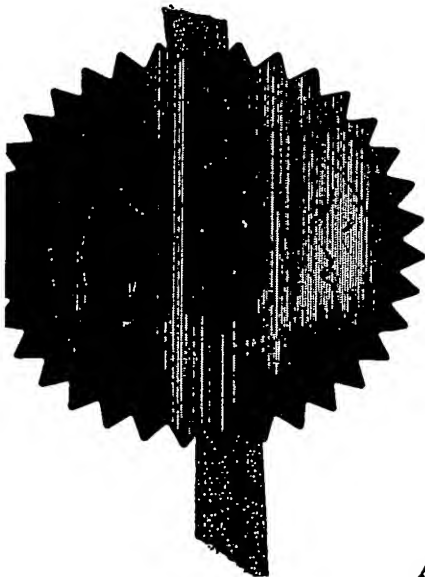
I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

BEST AVAILABLE COPY



Signed

*Stephen Hordley*

Dated

10 May 2004

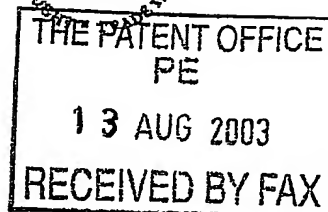
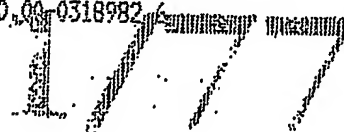
**PRIORITY  
DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

**Patents Form 1/77**

Patents Act 1977  
Rule 16)



13AUG03 E829898-1 D01091  
P01/7700 0.00-0318982.6



The Patent Office

Cardiff Road  
Newport  
South Wales  
NP10 8QQ

**Request for grant of a patent**

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference

AA 1649 GB

2. Patent application number

(The Patent Office will fill in this part)

0318982.6

3. Full name, address and postcode of the or of each applicant (underline all surnames)

JOHNSON MATTHEY PUBLIC LIMITED COMPANY  
2-4 COCKSPUR STREET  
TRAFALGAR SQUARE  
LONDON SW1 5BQ

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

GB

536262007

4. Title of the invention

METHOD OF DECOMPOSING NITROGEN DIOXIDE

5. Name of your agent (if you have one)

ANDREW DOMINIC NUNN

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

JOHNSON MATTHEY TECHNOLOGY CENTRE  
BLOUNTS COURT  
SONNING COMMON  
READING RG4 9NH

Patents ADP number (if you know it)

5583206001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

GB

0308944.8

17 April 2003

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

See note (d))

# Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	0
Description	12
Claim(s)	5
Abstract	1
Drawing(s)	8

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent (Patents Form 7/77)	
Request for preliminary examination and search (Patents Form 9/77)	ONE
Request for substantive examination (Patents Form 10/77)	
Any other documents (please specify)	

11.

I/We request the grant of a patent on the basis of this application.

Signature

*Andrew Nunn*

Date

13/8/03

A D NUNN

12. Name and daytime telephone number of person to contact in the United Kingdom

MRS F E STRANGE 0118 924 2125

## Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

## Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

## DECOMPOSING INTERNAL COMBUSTION ENGINE EXHAUST NO<sub>2</sub>

relates to a method of decomposing nitrogen dioxide (NO<sub>2</sub>) in a exhaust gas mixture of an internal combustion engine.

Internal combustion engines emit a mixture of pollutants (CO, unburned hydrocarbons (HC), nitrogen oxides (NO<sub>x</sub>) and NO<sub>x</sub> component can decompose into nitrogen monoxide (NO) and level of these pollutants in exhaust gases from internal combustion engine to atmosphere is regulated by legislation. Such legislation engine management, exhaust gas aftertreatment, and other measures.

One primary for treating exhaust gas comprises an oxidation catalyst that converts exhaust gas to NO<sub>2</sub> and a particulate filter for trapping PM. A catalyst that uses this arrangement is described in EP 03 41382 or US 6,340,000 which are incorporated herein by reference. The process comprises a diesel exhaust gas, containing PM and NO, is filtered over an oxidation catalyst to convert NO to NO<sub>2</sub>, collecting PM on the filter and regenerating the filter by oxidizing the NO<sub>2</sub>. This technology is commercially available as Johnson Matthey's Catalytic Trap or CRT®. Oxidation of the PM in the NO<sub>2</sub> results in a reaction leading to the complete oxidation of the PM to CO<sub>2</sub> and H<sub>2</sub>O as NO<sub>2</sub> is reduced to N<sub>2</sub> and H<sub>2</sub>O.

One process is that it is possible to combust diesel soot at temperatures of diesel soot in oxygen occurs at about 500°C and above. Exhaust gas is generally too cool to burn soot from gasoline engines on the filter causing a back-pressure problem in the system if combustion of soot in oxygen occurs without the provision of additional means to raise the temperature; so-called "active" regeneration regimes.

The process described in EP 03 41382 is such that, as exhaust emission levels are reduced by legislation, it is permissible to allow more NO<sub>2</sub> to be emitted into the atmosphere. For example,

the California Air Resources Board (CARB) has proposed that a maximum of 20% of tailpipe NO<sub>x</sub> of the relevant drive cycle is emitted as NO<sub>2</sub>. NO<sub>2</sub> is toxic and can cause headaches, dizziness and nausea in low doses. It also has an objectionable smell. If there is insufficient PM on the filter to react with NO<sub>2</sub> generated over the oxidation catalyst or the temperature of the exhaust gas is below a preferred range for combustion of PM in NO<sub>2</sub>, NO<sub>2</sub> can slip past the filter and be undesirably exhausted to atmosphere.

This problem is particularly acute when internal combustion engines are used in confined spaces, such as mines, where vehicles are used to drill for, load, and transport mined material to the surface. Many mining operations generate particulate matter, and so exhaust aftertreatment systems comprising filters for reducing the levels of PM emitted are being considered. Furthermore, explosives used to blast rock to recover a desired ore can generate NO<sub>2</sub>. Accordingly, it would be an advantage to reduce the exhaust gas emissions of both PM and NO<sub>2</sub> to the atmosphere in closed environments to improve the health and safety of miners. Indeed, the US Mine Safety and Health Administration prevents the use of diesel exhaust systems comprising diesel particulate filter systems that increase NO<sub>2</sub> emissions.

In selective catalytic reduction (SCR) by hydrocarbons (HC), HC react with NO<sub>x</sub>, rather than with O<sub>2</sub>, to form nitrogen, CO<sub>2</sub> and water according to equation (1):



The competitive, non-selective reaction with oxygen is given by Equation (2):



Two preferred groups of HC-SCR catalysts to selectively promote the desired reaction (1) for catalysing HC-SCR of NO<sub>x</sub> (HC-SCR catalysts are also referred to as "lean NO<sub>x</sub> catalysts" (LNC), "DeNO<sub>x</sub> catalysts", "NO<sub>x</sub> occluding catalysts", "NO<sub>x</sub> reducing catalysts" and even "non-selective catalytic reduction catalysts" (because they can catalyse non-selective reactions e.g. Equation (2)). These two preferred groups are platinum on alumina and copper-substituted zeolite such as Cu/ZSM-5.

Pt-based catalysts tend to operate at relatively low temperature (peak activity  $\sim 250^{\circ}\text{C}$ ) and have a relatively narrow temperature window for HC-SCR activity whereas zeolite-based HC-SCR catalysts have a wider temperature window than Pt-based HC-SCR catalysts and operate at higher temperatures (peak activity  $\sim 400^{\circ}\text{C}$ ).

5

One potential solution to this problem is described in EP 0758713, where in one embodiment, an exhaust system comprises an optionally platinum-based oxidation catalyst and a diesel particulate filter (DPF) in the CRT<sup>®</sup> configuration and a NO<sub>x</sub> absorbent downstream of the DPF. The NO<sub>x</sub> absorbent can comprise platinum for oxidising NO to NO<sub>2</sub> in  $\lambda > 1$  exhaust gas compositions, rhodium for reducing NO<sub>x</sub> to N<sub>2</sub> in  $\lambda < 1$  exhaust gas compositions and at least one substance selected from alkali metals such as potassium and caesium; alkali-earth metals such as barium and calcium; and rare-earth metals such as lanthanum for absorbing the NO<sub>2</sub> and storing it as the nitrate. Catalyst compositions comprising platinum, rhodium and a NO<sub>x</sub> absorbent material are typically called NO<sub>x</sub> traps.

15

In a second embodiment, a NO<sub>x</sub> reducing catalyst is disposed downstream of the filter for catalysing the reduction of the NO<sub>x</sub> to N<sub>2</sub> using diesel HC fuel and CO. The NO<sub>x</sub> reducing catalyst can be a zeolite such as ZSM-5 ion exchanged with copper or iron, or mordenite supporting platinum. However, it is clear from EP 0758713 that HC reductant for reducing the NO<sub>x</sub> is introduced into the exhaust system either by injecting additional fuel during the exhaust cycle or directly into the exhaust passage. In either case, injection is done always upstream of the CRT<sup>®</sup> oxidation catalyst.

20

In our WO 03/037507, we describe an exhaust system for an internal combustion engine comprising a catalyst, such as a platinum-based catalyst, for oxidising NO to NO<sub>2</sub> when the exhaust gas composition is  $\lambda > 1$ ; and a filter disposed downstream of the NO oxidation catalyst, i.e. in the CRT<sup>®</sup> configuration. The filter can comprise an oxidation catalyst such as platinum and/or palladium, rhodium and a NO<sub>x</sub> absorbent material, such as any of those described in EP 0758713 above. The filter component *per se* of this arrangement is described in Japanese patent no. 2722987.

25

30

We have investigated ways of catalytically decomposing NO<sub>2</sub> to NO and we have found that, very surprisingly, certain known HC-SCR catalysts are particularly active. In order to optimise conversion, we found that a small amount of HC reductant is desirable. However,

whilst our results show that a small amount of reduction to  $N_2$  is effected, very good  $NO_2$  conversion to NO can be achieved. It will be noted that for HC-SCR, HC: $NO_x$  ratios of from between 2 to 6 are preferred in the above-mentioned temperature windows. Our results show that  $NO_2$  decomposition can be effected at much lower temperatures and HC: $NO_x$  ratios.

According to a first aspect, the invention provides a method of decomposing nitrogen dioxide ( $NO_2$ ) in an exhaust gas of a lean-burn internal combustion engine, which method comprising adjusting the HC: $NO_x$  ratio of the exhaust gas to from 0.1 to 2 and contacting this gas mixture with at least one support comprising at least one metal selected from the group consisting of rhodium, silver, iron and copper.

$NO_2$  can account for up to about 50%  $NO_x$  in the exhaust gas of an internal combustion engine. Therefore, according to one embodiment the HC: $NO_2$  ratio is adjusted to from 0.05 to 1.

We have found that for the prescribed HC: $NO_x$  ratios,  $NO_2$  conversion is reduced at lower temperatures. In order to meet the proposed CARB threshold of a maximum of 20%  $NO_2$  of  $NO_x$  emitted, in one embodiment we prefer that the step of adjusting the HC: $NO_x$  ratio is performed only when the exhaust gas temperature is at 250°C and above. It will be noted that  $NO_2$  conversion is possible at temperatures much below that required for HC-SCR for a similar catalyst i.e. above 250°C for  $NO_2$  conversion vs. about 400°C for HC-SCR over Fe-Beta zeolite.

According to a further embodiment, the step of adjusting the HC: $NO_x$  ratio is done when the exhaust gas temperature is in a range that has been pre-determined to produce increased  $NO_2$  in the exhaust system. Such temperature range will usually depend on the engine type and the duty of the vehicle. Illustrative embodiments include city centre buses comprising heavy duty diesel engines (250 - 300°C); buses in non-city centre locations (up to 400°C); and heavy duty diesel trucks (up to 500°C).

Potentially, the method according to the first aspect of the invention can be used to treat gas mixtures including  $NO_2$  generated by any chemical, e.g. industrial, process. However, for the purposes of the present invention, the method is for treating an exhaust gas mixture derived from combustion of a hydrocarbon fuel, such as diesel fuel, gasoline fuel, natural gas (NG) or liquid petroleum gas (LPG) in an internal combustion engine.



According to a second aspect, the invention provides an exhaust system for an internal combustion engine, which system comprising a catalyst for decomposing  $\text{NO}_2$  with a suitable reductant, and means, in use, for adjusting the  $\text{HC}:\text{NO}_x$  ratio in an exhaust gas upstream of the catalyst to from 0.1 to 2, which catalyst comprising at least one support comprising at least one metal selected from the group consisting of rhodium, silver, iron and copper.

In one embodiment, the means for adjusting is adapted to adjust the  $\text{HC}:\text{NO}_2$  ratio of the exhaust gas to from 0.05 to 1.

According to a further embodiment, the adjustment means is controlled, in use, to operate when the exhaust gas temperature is above  $250^\circ\text{C}$ .

In another embodiment, the adjustment means is controlled, in use, to operate when the exhaust gas temperature is below  $500^\circ\text{C}$ .

Control of the adjustment means can be effected by suitable means comprising, in one embodiment, a processor which in turn can form part of the engine control unit (ECU) if desired.

In order to control the  $\text{HC}:\text{NO}_x$  ratio, it is desirable that the system comprises one or more sensors for inputting the status of one or more of the following conditions in the system: exhaust gas temperature; catalyst bed temperature; exhaust gas mass flow;  $\text{NO}_2$  in the exhaust gas, e.g. as detected by a suitable  $\text{NO}_2$  sensor; manifold vacuum; ignition timing; engine speed; throttle position; lambda value of the exhaust gas composition; quantity of fuel injected in the engine; position of an exhaust gas circulation valve; and boost pressure.

It will be understood that the  $\text{HC}:\text{NO}_x$  ratio can be varied according to the or each input received. For example, at lower exhaust gas temperatures a higher ratio is desirable for a pre-determined  $\text{NO}_2$  conversion, whereas a lower  $\text{HC}:\text{NO}_2$  ratio can be used at higher temperatures.

According to another embodiment, the control means is operated according to stored look-up tables or an engine map in response to at least one of the above inputs.

Adjustment of the  $\text{HC}:\text{NO}_x$  ratio to within the prescribed range can be done either by increasing the amount of  $\text{HC}$  or by adjusting the  $\text{NO}_x$  e.g. by adjusting the amount of exhaust gas



5

b

5

5

According to a further embodiment, the oxidation catalyst is associated with a  $\text{NO}_x$  absorbent material. One such arrangement is that the  $\text{NO}_x$  absorbent material, typically at least one compound of an alkali metal e.g. potassium or caesium, at least one compound of an alkaline earth metal, such as barium, strontium or calcium, or at least one compound of a rare earth metal, for example lanthanum or yttrium, is associated with the oxidation catalyst. Generally, the compounds will be oxides but, in use, the compounds may also be present as hydroxides, carbonates or, following  $\text{NO}_x$  absorption (as will be described hereinafter) nitrates.

In this arrangement,  $\text{NO}_2$  generated over the oxidation catalyst during  $\lambda > 1$  conditions can be absorbed in the  $\text{NO}_x$  absorbent material and stored as the nitrate. Since the  $\text{NO}_x$  absorbent material has a finite capacity to absorb  $\text{NO}_x$ , it is necessary periodically to regenerate it, i.e. to remove the stored  $\text{NO}_x$ . Generally, this is done in practice by transiently adjusting the  $\lambda$  composition of the exhaust gas to the rich side, i.e.  $\lambda < 1$ , for example by introducing additional HC fuel into the exhaust gas or by allowing less air into the combustion mixture. The nitrate forms of the alkali, alkaline earth and rare earth metals are understood to be unstable in rich exhaust gas, and so  $\text{NO}_x$  is released, in what is believed to be a mixture of at least NO and  $\text{NO}_2$ .

Typically, compositions comprising  $\text{NO}_x$  absorbent materials also comprise rhodium for reducing the  $\text{NO}_x$  to  $\text{N}_2$  in the presence of the reductant. However, the rhodium  $\text{NO}_2$  decomposition catalysts of the present invention do not include other PGM's such as platinum and/or palladium commonly used as oxidation catalysts. In one arrangement, for example, the  $\text{NO}_2$  decomposition catalyst is on a separate monolith downstream of the filter. In a particular embodiment, however, the  $\text{NO}_2$  decomposition catalyst can be disposed on a downstream end of the filter.

The filter can be any suitable substrate including a wall-flow filter of ceramic material such as silicon carbide or cordierite. Alternatively, it can be the device described in either EP 1057519 or WO 03/038248.

In one embodiment the at least one support for use in the  $\text{NO}_2$  decomposition catalyst is selected from alumina, ceria, zirconia, titania, silica, chromia, a zeolite or a mixture, composite oxide or mixed oxide of any two or more thereof.

"Composite oxide" as defined herein means a largely amorphous oxide material comprising oxides of at least two elements which are not true mixed oxides consisting of the at least two elements.

5 In a further embodiment, the composite oxide or mixed oxide is selected from silica-alumina, a silica-zirconia, alumina-zirconia, alumina-chromia, alumina-ceria, ceria-titania or ceria-zirconia.

10 Examples of suitable zeolite components for the NO<sub>2</sub> decomposition catalysts are ZSM-5,  $\beta$ -zeolite, Y-zeolite or mordenite.

15 In each case, the support can be doped with at least one of lanthanum, barium, cerium, tungsten, silica and manganese to improve the stability of the support to high temperature ageing, act as a promoter in the decomposition of NO<sub>2</sub> and/or improve the oxygen storage capacity of the system, particularly in the case of manganese.

20 The NO<sub>2</sub> decomposition catalysts can be prepared according to known methods such as wet impregnation of the at least one support material using a suitable metal salt followed by calcination, or by ion exchange.

In one embodiment, the at least one support for use in the exhaust system according to the invention can comprise from 0.1 to 5.0 wt% rhodium, such as from 0.25 to 2.5 wt% rhodium, based on the total weight of the support.

25 In a specific embodiment, the catalyst comprises 0.5 wt% rhodium supported on alumina.

30 An important feature of the invention is that the support on which the rhodium is supported is devoid of other platinum group metals. Furthermore, the supported rhodium is not mixed with other support(s) supporting non-rhodium PGMs. Put another way, the supported rhodium is segregated from non-rhodium PGMs present in the exhaust system.

The method and exhaust system of the present invention are different from those described in EP 0758713 and PCT/GB02/004750 in that in the prior art, the rhodium is a component in a NO<sub>x</sub> trap composition, i.e. it is associated with other catalysts such as platinum

and NO<sub>x</sub> absorbent materials such as potassium, caesium and calcium. Furthermore, it is understood from the description of e.g. EP-A-1079084 discussed in PCT/GB02/004750 that any rhodium present would be on the upstream end of the filter.

5 In a further embodiment, the at least one support comprises from 1 to 10 wt% copper, such as from 2.5 to 7.5 wt% copper, based on the total weight of the support. Where the at least one support comprises a zeolite, it can be impregnated or ion exchanged onto the support.

10 In a further embodiment, the at least one support comprises from 1 to 10 wt% iron, such as from 2.5 to 7.5 wt% iron, based on the total weight of the support. Where the at least one support comprises a zeolite, it can be impregnated or ion exchanged onto the support.

In a specific embodiment the catalyst comprises 5 wt% iron and the at least one support is zeolite ZSM-5 and/or  $\beta$ -zeolite.

15

According to a further embodiment, the at least one support comprises from 0.1 to 5.0 wt% silver, such as from 0.25 to 2.5 wt% silver, based on the total weight of the support.

20 In a specific embodiment, the catalyst comprises particulate ceria mixed with 2 wt% silver supported on alumina in a weight ratio of 1:4.

25 According to a third aspect, the invention provides an internal combustion engine comprising an exhaust system according to the invention. Such engine can be fuelled by any suitable fuel such as diesel fuel, gasoline fuel, natural gas (NG) or liquid petroleum gas (LPG).

According to a fourth aspect, the invention provides a vehicle, such as a mining vehicle, comprising an engine according to the third aspect of the invention.

30 It is believed that the NO<sub>2</sub> decomposition catalysts described herein, in addition to catalysing the reduction of NO<sub>2</sub>, may also catalyse the reduction of SO<sub>3</sub> to SO<sub>2</sub> in exhaust gas conditions and can be used where such reaction is desirable, e.g. to reduce the amount of SO<sub>3</sub>-derived particulate observed in diesel drive cycles.

In order that the invention may be more fully understood, the following Examples are provided by way of illustration only and with reference to the accompanying drawings, in which:

Figure 1 is a graph showing %NO<sub>2</sub> conversion as a function of temperature (°C) for NO<sub>2</sub> decomposition catalysts with and without diesel fuel injection (about 120ppm C1 (MK1)) relative to a blank reactor control; and

Figure 2 is a graph showing NO production from NO<sub>2</sub> in the presence of diesel fuel as a function of temperature relative to a blank reactor control;

Figure 3 is a graph showing NO<sub>2</sub> decomposition over a Cu/Beta-zeolite catalyst at HC:NO<sub>2</sub> of 0.5 as a function of temperature;

Figure 4 is a graph showing %NO<sub>2</sub> conversion over a Cu/Beta-zeolite catalyst at HC:NO<sub>2</sub> of 0.5 as a function of temperature;

Figure 5 is a graph showing NO<sub>2</sub> / NO<sub>x</sub> ratio (%) over a Cu/Beta-zeolite catalyst at HC:NO<sub>2</sub> of 0.5 as a function of temperature;

Figure 6 is a graph showing NO<sub>2</sub> decomposition over a Cu/Beta-zeolite catalyst at HC:NO<sub>2</sub> of 0.25 as a function of temperature;

Figure 7 is a graph showing NO<sub>2</sub> / NO<sub>x</sub> ratio (%) over a Cu/Beta-zeolite catalyst at HC:NO<sub>2</sub> of 0.25 as a function of temperature; and

Figure 8 is a graph showing NO<sub>2</sub> / NO<sub>x</sub> ratio (%) over a Cu/Beta-zeolite catalyst at HC:NO<sub>2</sub> of 0.25 as a function of temperature.

### Example 1

A series of catalysts were analysed on a simulated catalyst activity test (SCAT) gas rig for their abilities to decompose NO<sub>2</sub> in a simulated exhaust gas reaction mixture that contains 200ppm NO<sub>2</sub>, about 120ppm C1 diesel fuel (MK1), 12% O<sub>2</sub>, 4.5% CO<sub>2</sub>, 4.5% H<sub>2</sub>O and 20ppm SO<sub>2</sub>, N<sub>2</sub> balance. Each catalyst was heated in a 10°C-a-minute ramp in the reaction mixture from

150°C to 500°C. The catalysts tested were 5 wt% ion exchanged ZSM-5 zeolite ((by total weight of the support) 5Cu/ZSM5), 0.5 wt% rhodium on alumina ((by total weight of the particulate support) 0.5Rh/Al<sub>2</sub>O<sub>3</sub>) and 5 wt% ion exchanged  $\beta$ -zeolite ((by total weight of the support) 5Cu/Beta).

5

As a control, NO<sub>2</sub> decomposition over the blank reactor with mesh was measured and the 5Cu/ $\beta$ -zeolite catalyst was tested with the above mixture but in the absence of diesel fuel. As a further test, the 5 wt% ion exchanged ZSM-5 zeolite was tested in the above exhaust gas reaction mixture wherein the 200ppm NO<sub>2</sub> was exchanged for 100ppm NO and 100ppm NO<sub>2</sub>, i.e. 1:1 NO:NO<sub>2</sub>. The results of NO<sub>2</sub> decomposition and NO production from NO<sub>2</sub> are set out in Figures 1 and 2.

10

It can be seen that the addition of diesel improves the low temperature conversion of NO<sub>2</sub> to NO. The 5Cu/ $\beta$ -zeolite catalyst is the most active catalyst giving 100% NO<sub>2</sub> removal from 200 to 350°C.

15

Changing the gaseous NO<sub>x</sub> composition from 200ppm NO<sub>2</sub> to 100ppm NO/100ppm NO<sub>2</sub> has no perceptible effect on the low temperature performance, although the activity does fall off more sharply at the high temperature end when using the NO/NO<sub>2</sub> mix. Whether this is due to NO inhibition (perhaps unlikely at this high temperature) or is a kinetic/reaction order effect associated with reducing the inlet NO<sub>2</sub> concentration from 200 to 100ppm is not yet clear.

20

The mass balances for NO<sub>2</sub> decomposition vs. NO production at temperatures in the 300-400°C range do not correlate. For example, at 350°C the NO<sub>2</sub> removal is 100%, but only around 150ppm NO is seen in the gas phase (instead of the 200ppm which we would expect to see if all of the NO<sub>2</sub> was being decomposed to NO). We believe, therefore, that we are getting some lean NO<sub>x</sub> reduction here, using stored HC and gas phase HC to remove the NO<sub>x</sub> - the temperature window fits with this hypothesis.

25

30

### Example 2

In a laboratory, a bench mounted, heavy-duty diesel engine fitted with a CRT<sup>®</sup> exhaust gas after-treatment system as described in EP 0341832, i.e. a platinum on aluminium based oxidation catalyst for oxidising NO to NO<sub>2</sub> and a ceramic wall-flow diesel particulate filter, was

used to test the principle of  $\text{NO}_2$  decomposition shown in Example 1 in "real-world" conditions. A diesel fuel injector was disposed downstream of the filter and a ceramic monolith of 400 cells per square inch ( $62 \text{ cells cm}^{-2}$ ) was coated with a  $5\text{Cu} / \text{Beta-zeolite}$  catalyst of Example 1.

5         $\text{NO}$  and  $\text{NO}_2$  sensors were used to detect the amounts of these gases at various points in the exhaust system, and the amounts of detected  $\text{NO}_2$  were used to calculate an amount of diesel fuel to be injected to obtain an  $\text{HC}:\text{NO}_2$  ratio of 0.5 and 0.25 over the catalyst. (Since approximately 50% of  $\text{NO}_x$  downstream of the  $\text{CRT}^{\text{®}}$  oxidation catalyst at up to about  $400^\circ\text{C}$  is  $\text{NO}_2$ , these values correlate to an  $\text{HC}:\text{NO}_x$  ratio of approximately 1.0 and 0.5 respectively). The  
10        engine load was adjusted to increase temperature in the exhaust system and measurements were made after the system had been run at steady state conditions.

Figures 3 – 5 show the results for  $\text{HC}:\text{NO}_2$  of 0.5. In the legends, the  $\text{NO}_2$  decomposition catalyst is referred to as a "clean-up" catalyst. It can be seen that good  $\text{NO}_2$  decomposition  
15        activity is observed, although the %  $\text{NO}_2$  decomposition does fall off at temperatures below about  $300^\circ\text{C}$ . A small amount of  $\text{NO}_x$  conversion of 7% peak at about  $325^\circ\text{C}$  is observed (results not shown). Under the conditions used,  $\text{NO}_2/\text{NO}_x$  is below 20% at every temperature except the lowest ( $250^\circ\text{C}$ ). The fall off in  $\text{NO}_2/\text{NO}_x$  ratio after the  $\text{CRT}^{\text{®}}$  oxidation catalyst is due to the thermodynamic equilibrium favouring  $\text{NO}$  over  $\text{NO}_2$ . Negligible  $\text{HC}$  slip was observed (results  
20        not shown).

At  $\text{HC}:\text{NO}_2$  of 0.25 (results shown in Figures 6 – 8), good  $\text{NO}_2$  decomposition is still observed, but the conversion peaks at 80%. Again, a small amount of  $\text{NO}_x$  conversion (peak 6% at  $325^\circ\text{C}$ ) was seen. Under the conditions used,  $\text{NO}_2/\text{NO}_x$  is below 20% at temperatures above  
25         $325^\circ\text{C}$ . Negligible  $\text{HC}$  slip was observed.



CLAIMS:

1. A method of decomposing nitrogen dioxide ( $\text{NO}_2$ ) in an exhaust gas of a lean-burn internal combustion engine, which method comprising adjusting the hydrocarbon : nitrogen oxides ( $\text{HC}:\text{NO}_x$ ) ratio of the exhaust gas to from 0.1 to 2 and contacting this gas mixture with at least one support comprising at least one metal selected from the group consisting of rhodium, silver, iron and copper.
2. A method according to Claim 1, wherein the  $\text{HC}:\text{NO}_2$  ratio is adjusted to from 0.05 to 1.
3. A method according to claim 1 or 2, wherein the step of adjusting the  $\text{HC}:\text{NO}_x$  ratio is done at above  $250^\circ\text{C}$ .
4. A method according to claim 3, wherein the step of adjusting the  $\text{HC}:\text{NO}_x$  ratio is done at up to  $500^\circ\text{C}$ .
5. A method according to claim 1, 2, 3 or 4, wherein the hydrocarbon is diesel fuel, gasoline fuel, natural gas (NG) or liquid petroleum gas (LPG).
6. An exhaust system for an internal combustion engine, which system comprising a catalyst for decomposing  $\text{NO}_2$  with a suitable reductant, and means, in use, for adjusting the hydrocarbon : nitrogen oxides ( $\text{HC}:\text{NO}_x$ ) ratio in an exhaust gas upstream of the catalyst to from 0.01 to 2, which catalyst comprising at least one support comprising at least one metal selected from the group consisting of rhodium, silver, iron and copper.
7. An exhaust system according to claim 6, wherein the means for adjusting is adapted to adjust the  $\text{HC}:\text{NO}_2$  ratio of the exhaust gas to from 0.05 to 1.
8. An exhaust system according to claim 6 or 7, wherein the adjustment means is controlled, in use, to operate when the exhaust gas temperature is above  $250^\circ\text{C}$ .
9. An exhaust system according to claim 8, wherein the adjustment means is controlled, in use, to operate when the exhaust gas temperature is below  $500^\circ\text{C}$ .

10. An exhaust system according to claim 6, 7, 8 or 9, wherein the adjustment means comprises a control means comprising a processor.
11. An exhaust system according to claim 10, wherein the processor is part of an engine control unit (ECU).
12. An exhaust system according to claim 10 or 11, wherein the control means adjusts the HC:NO<sub>x</sub> ratio in response to one or more of the following inputs: exhaust gas temperature; catalyst bed temperature; rate of exhaust gas mass flow; NO<sub>2</sub> in the exhaust gas; manifold vacuum; ignition timing; engine speed; throttle position; lambda value of the exhaust gas composition; quantity of fuel injected in the engine; position of an exhaust gas recirculation valve; and boost pressure.
13. An exhaust system according to claim 12, wherein the control means is operated according to stored look-up tables or an engine map in response to the at least one input.
14. An exhaust system according to any of claims 6 to 13, wherein the means for adjusting the HC:NO<sub>x</sub> ratio comprises at least one of: means for injecting a reductant into the exhaust gas; means for adjusting the ignition timing of at least one engine cylinder; means for adjusting fuel injection timing of at least one engine cylinder; means for adjusting the engine air-to-fuel ratio; and adjustment of exhaust gas recirculation rate.
15. An exhaust system according to any of claims 6 to 14, wherein where the at least one metal is rhodium, the support is free of other platinum group metals (PGMs).
16. An exhaust system according to any of claims 6 to 15, wherein the NO<sub>2</sub> decomposition catalyst is disposed downstream of an oxidation catalyst comprising at least one PGM, preferably at least one of platinum and palladium.
17. An exhaust system according to claim 16, wherein the oxidation catalyst is on a diesel particulate filter.
18. An exhaust system according to claim 17, wherein the oxidation catalyst is associated with a NO<sub>x</sub> absorbent material.

19. An exhaust system according to claim 16, 17 or 18, wherein the NO<sub>2</sub> decomposition catalyst is disposed on a downstream end of a filter.
- 5 20. An exhaust system according to any of claims 6 to 20, wherein the filter is a wall-flow filter.
- 10 21. An exhaust system according to any of claims 14 to 20, when appendant to claim 14 wherein the reductant injecting means introduces the reductant into the exhaust system upstream of the NO<sub>2</sub> decomposition catalyst and downstream of any PGM oxidation catalyst.
- 15 22. An exhaust system according to any of claims 6 to 21, wherein the at least one support comprises from 0.1 to 5.0 wt% rhodium based on the total weight of the at least one support.
- 20 23. An exhaust system according to claim 22, wherein the at least one support comprises from 0.25 to 2.5 wt% rhodium based on the total weight of the at least one support.
- 25 24. An exhaust system according to any of claims 6 to 21, wherein the at least one support comprises from 0.1 to 5.0 wt% silver based on the total weight of the at least one support.
26. An exhaust system according to claim 24, wherein the at least one support comprises from 0.25 to 2.5 wt% silver based on the total weight of the at least one support.
27. An exhaust system according to any of claims 6 to 21, wherein the at least one support comprises from 1 to 10 wt% copper based on the total weight of the support.
- 30 28. An exhaust system according to claim 26, wherein the at least one support comprises from 2.5 to 7.5 wt% copper based on the total weight of the at least one support.
29. An exhaust system according to any of claims 6 to 21, wherein the at least one support comprises from 1 to 10 wt% iron based on the total weight of the at least one support.

29. An exhaust system according to claim 28, wherein the at least one support comprises from 2.5 to 7.5 wt% iron based on the total weight of the at least one support.
30. An exhaust system according to any of claims 6 to 29, wherein the at least one support  
5 comprises alumina, ceria, zirconia, titania, silica, chromia, a zeolite or a mixture, composite oxide or mixed oxide of any two or more thereof.
31. An exhaust system according to claim 30, wherein the composite oxide or mixed oxide  
10 comprises silica-alumina, a silica-zirconia, alumina-zirconia, alumina-chromia, alumina-ceria, ceria-titania or ceria-zirconia.
32. An exhaust system according to claim 31, wherein the zeolite is ZSM-5,  $\beta$ -zeolite, Y-zeolite or mordenite.
- 15 33. An exhaust system according to any of the claims 6 to 32, wherein the at least one support and/or the particulate oxide material is doped with at least one of lanthanum, barium, cerium, tungsten, silica and manganese.
34. An exhaust system according to any of claims 6 to 33, wherein the catalyst comprises 5  
20 wt% copper and the at least one support is zeolite ZSM-5 and/or  $\beta$ -zeolite.
35. An exhaust system according to any of claims 6 to 34, wherein the catalyst comprises 5 wt% iron and the at least one support is zeolite ZSM-5 and/or  $\beta$ -zeolite.
- 25 36. An exhaust system according to any of claims 6 to 35, wherein the catalyst comprises 2 wt% silver supported on alumina.
37. An exhaust system according to any of claims 6 to 36, wherein the catalyst comprises 0.5  
30 wt% rhodium supported on alumina.
38. An internal combustion engine comprising an exhaust system according to any of claims 6 to 37.

39. An engine according to claim 38 fuelled with diesel fuel, gasoline fuel, natural gas (NG) or liquid petroleum gas (LPG).

40. A vehicle, such as a mining vehicle, comprising an engine according to claim 38 or 39.

5

41. A method of decomposing nitrogen dioxide ( $\text{NO}_2$ ) substantially as described herein.

42. An exhaust system substantially as described herein.

10 43. An internal combustion engine substantially as described herein.

ABSTRACT

5

METHOD OF DECOMPOSING NITROGEN DIOXIDE

10 A method of decomposing nitrogen dioxide in an exhaust gas of a lean-burn internal combustion engine comprises adjusting the hydrocarbon : nitrogen oxides (HC:NO<sub>x</sub>) ratio of the exhaust gas to from 0.1 to 2 and contacting this exhaust gas mixture with at least one support comprising at least one metal selected from the group consisting of rhodium, silver, iron and copper.

[Figure 1]

1/8

Effect of Diesel Fuel (120ppm C4) on NO<sub>2</sub> Decomposition

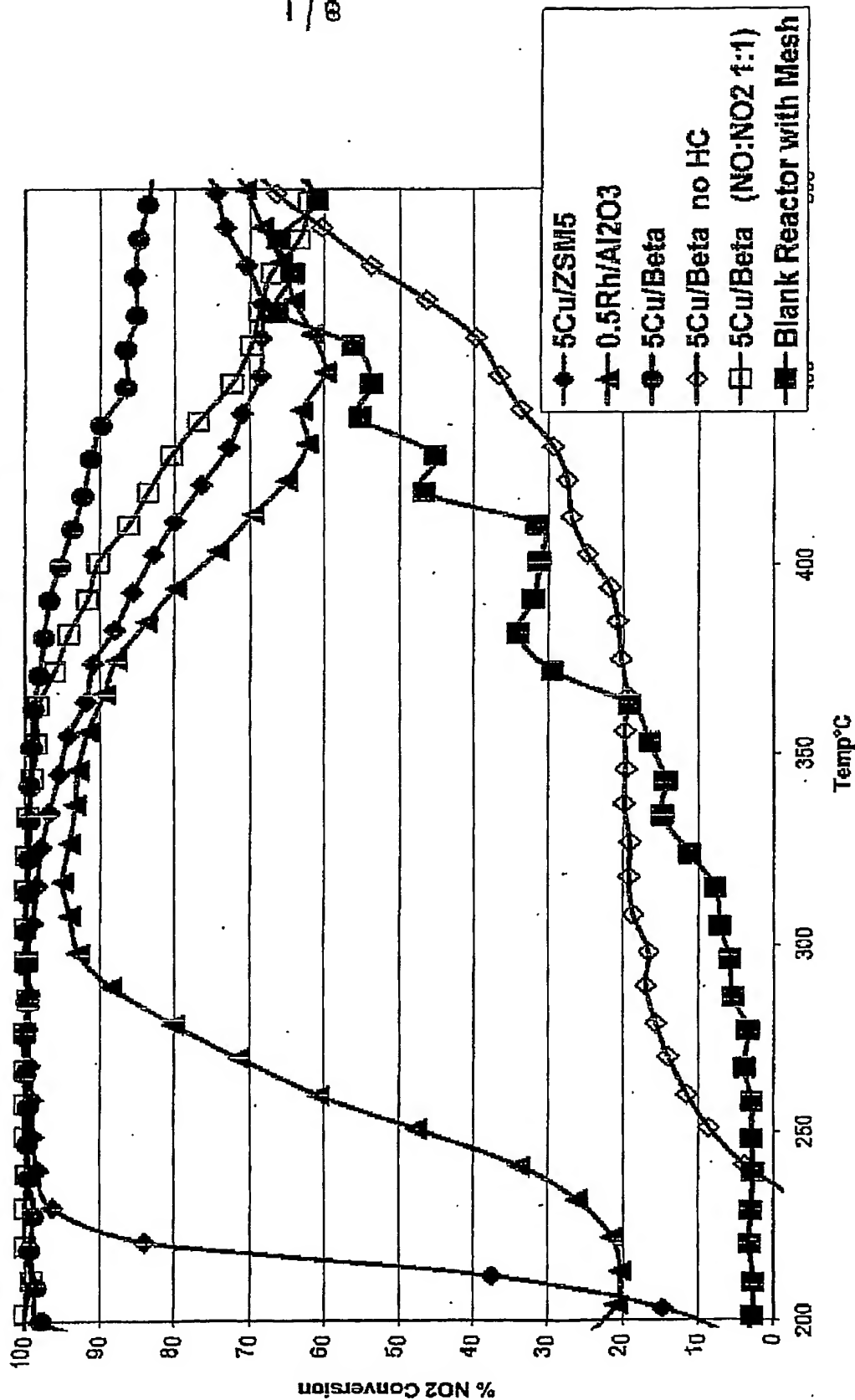


Fig 1.



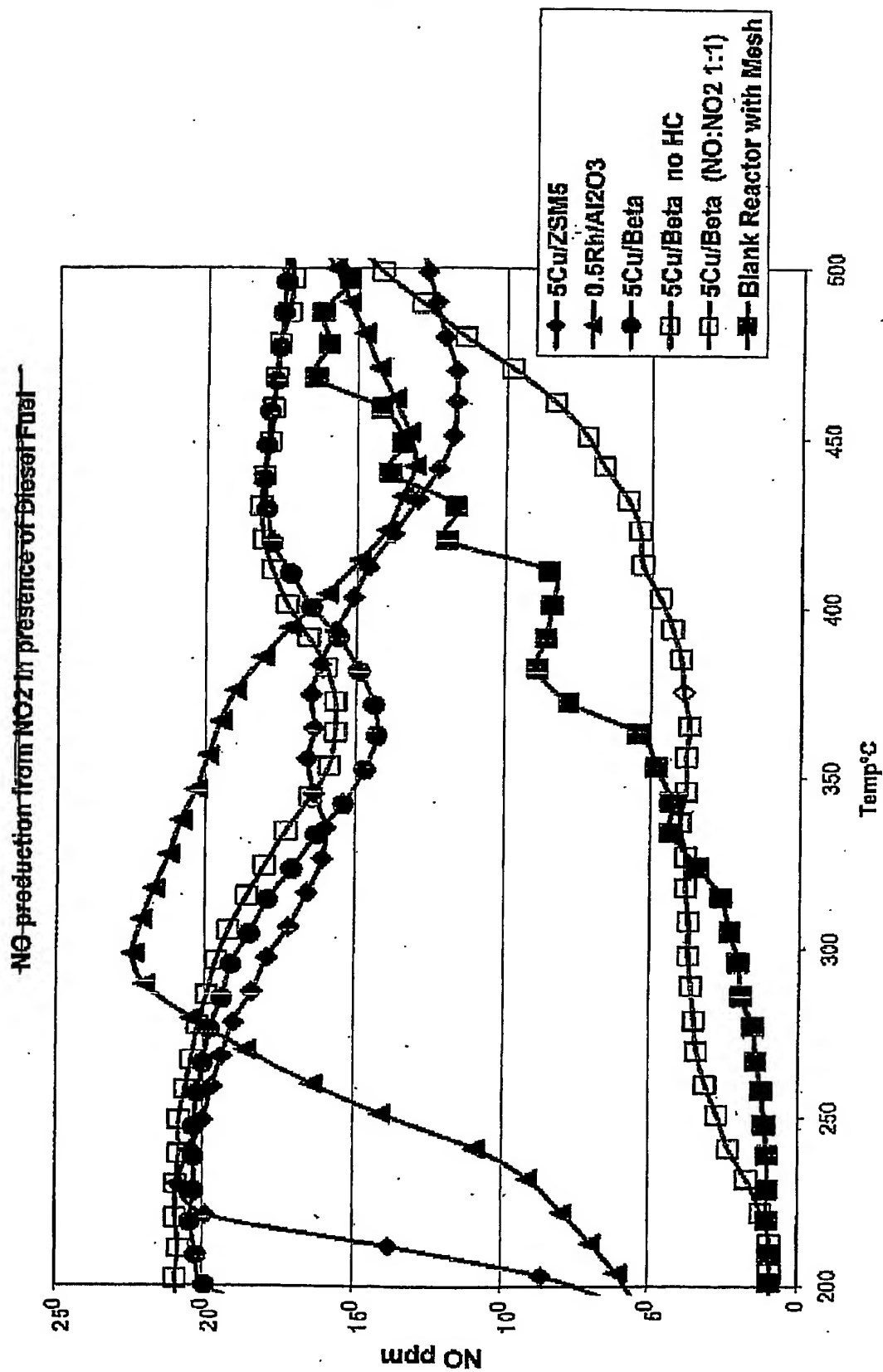


Fig 2.

3/8

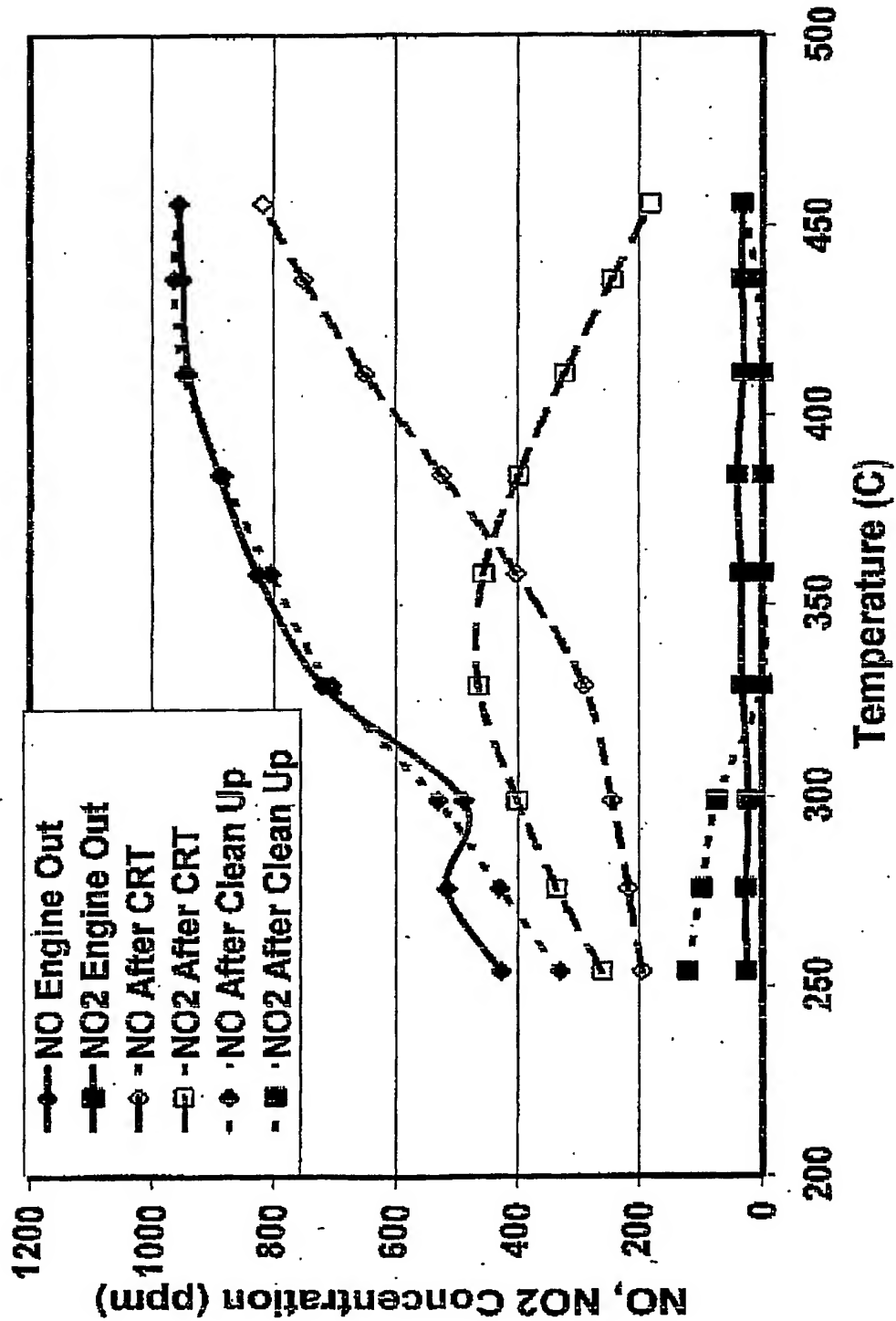


Fig 3.

4/8

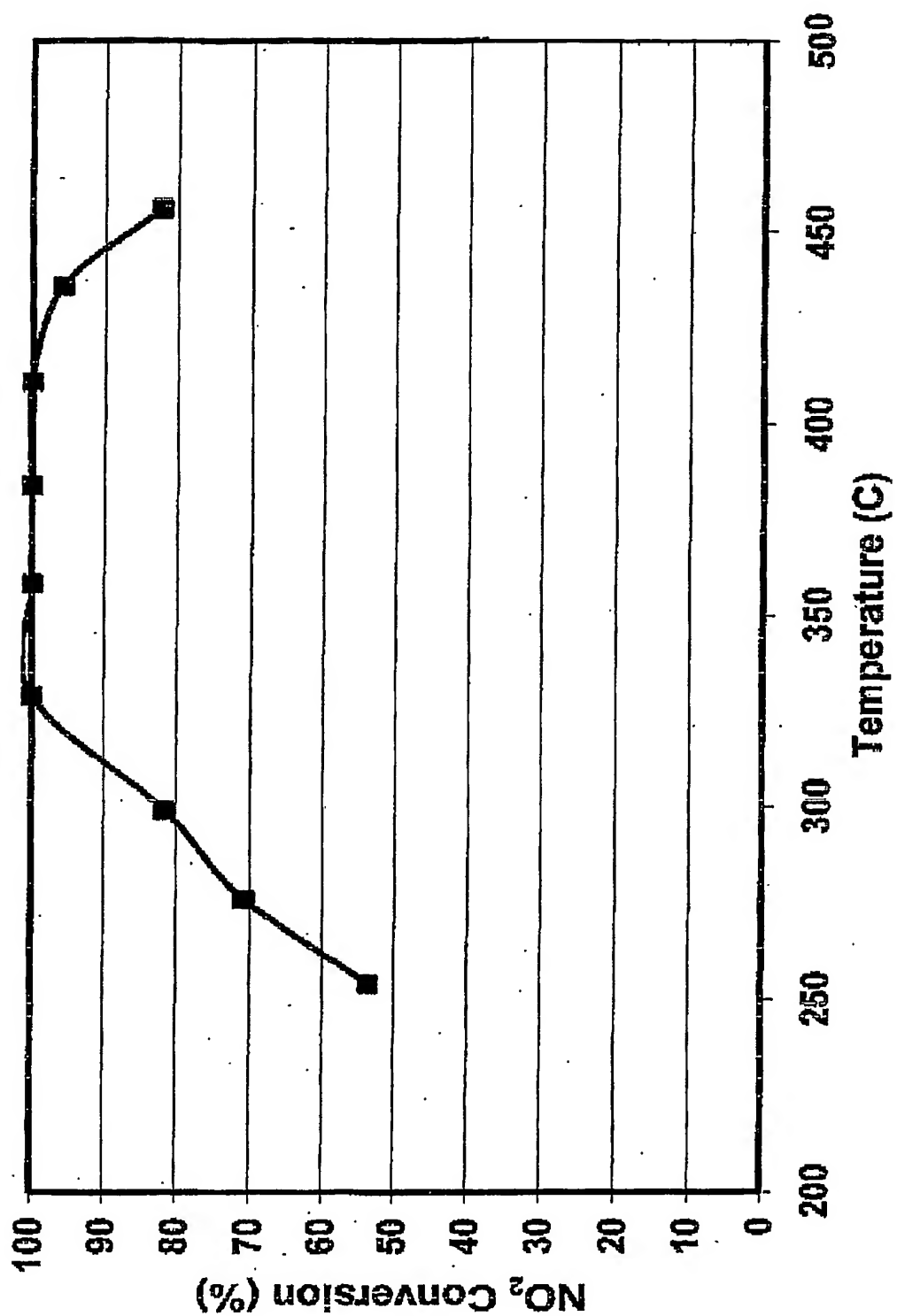


Fig 4.

5/8

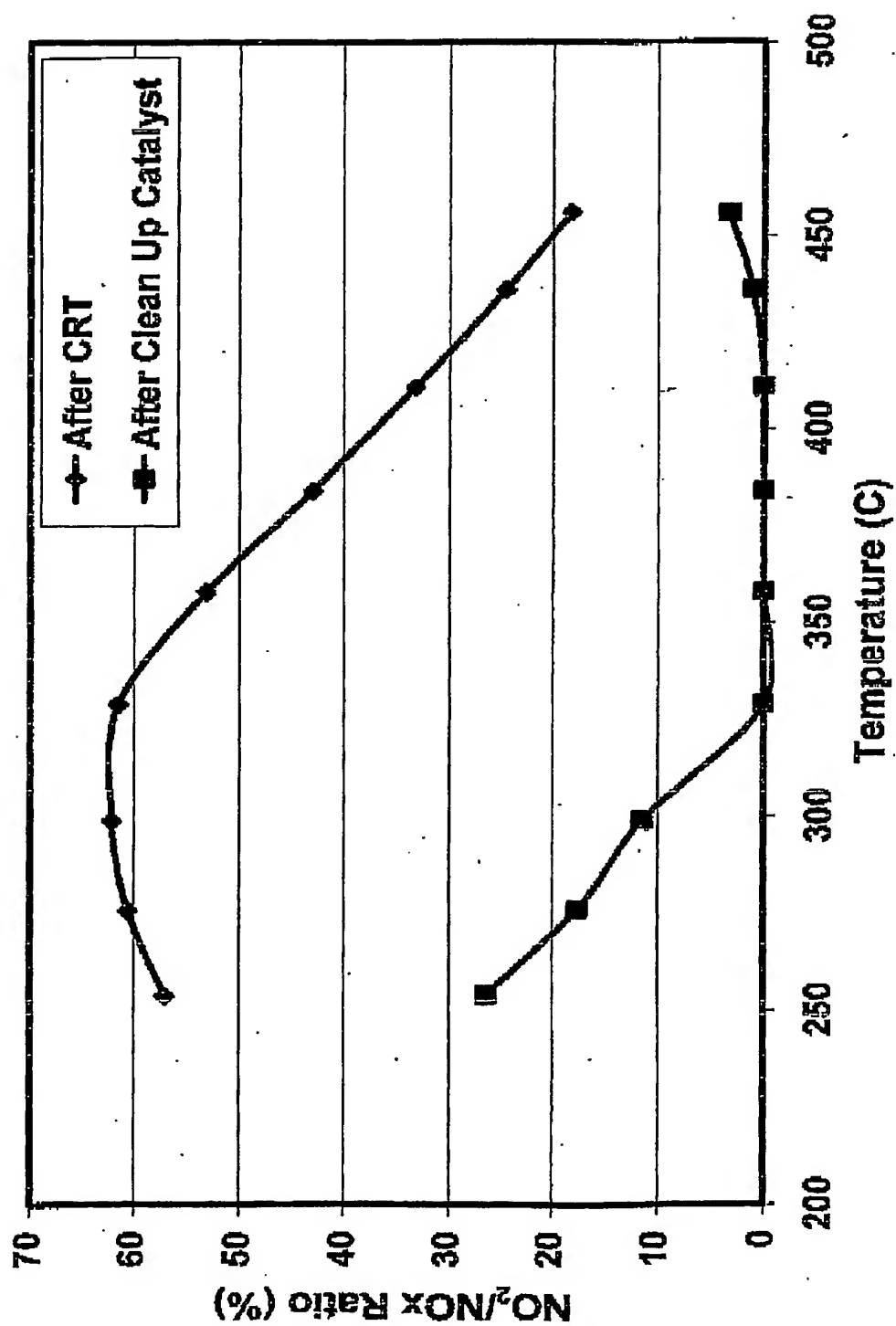


FIG. 5

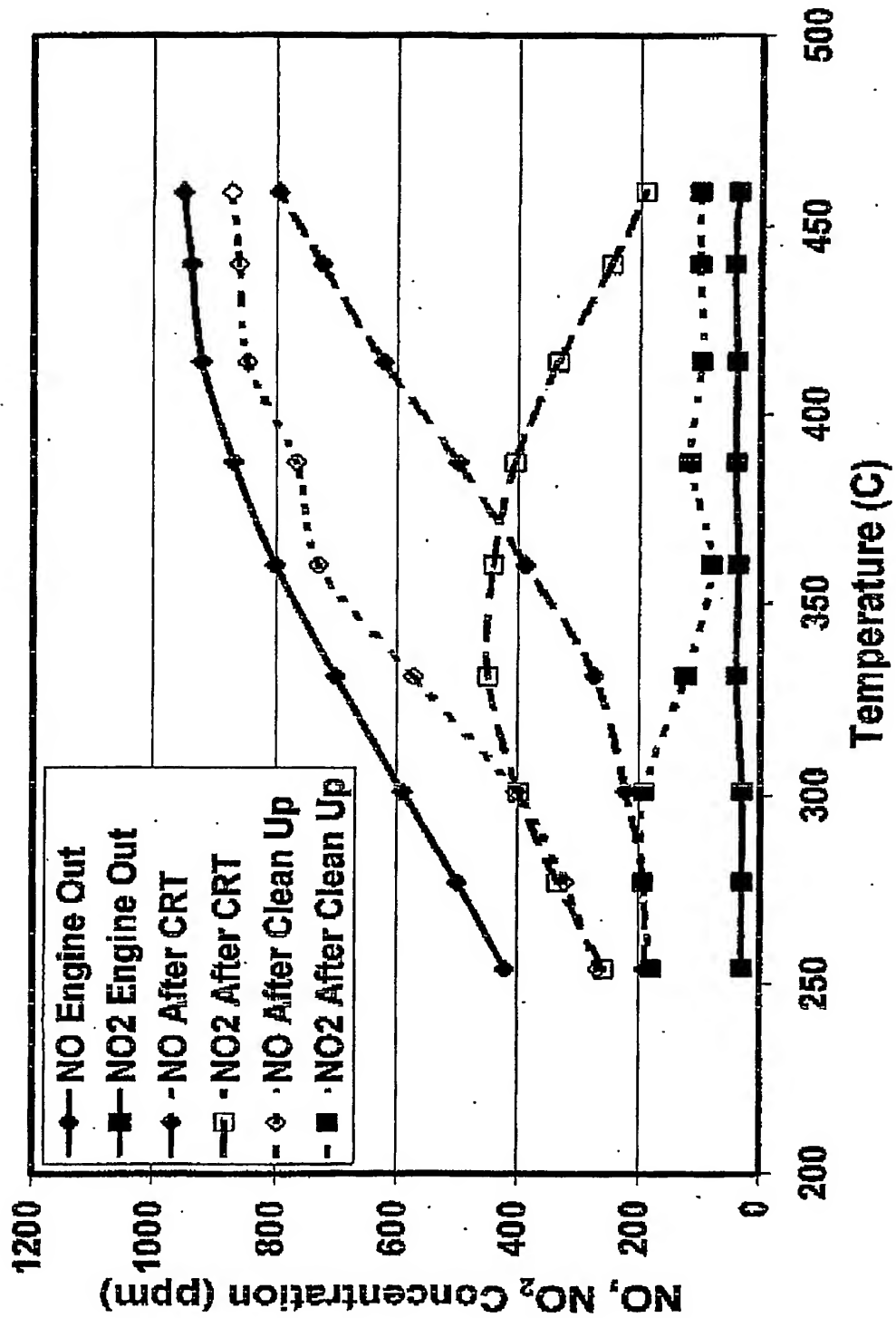


FIG 6.

7/8

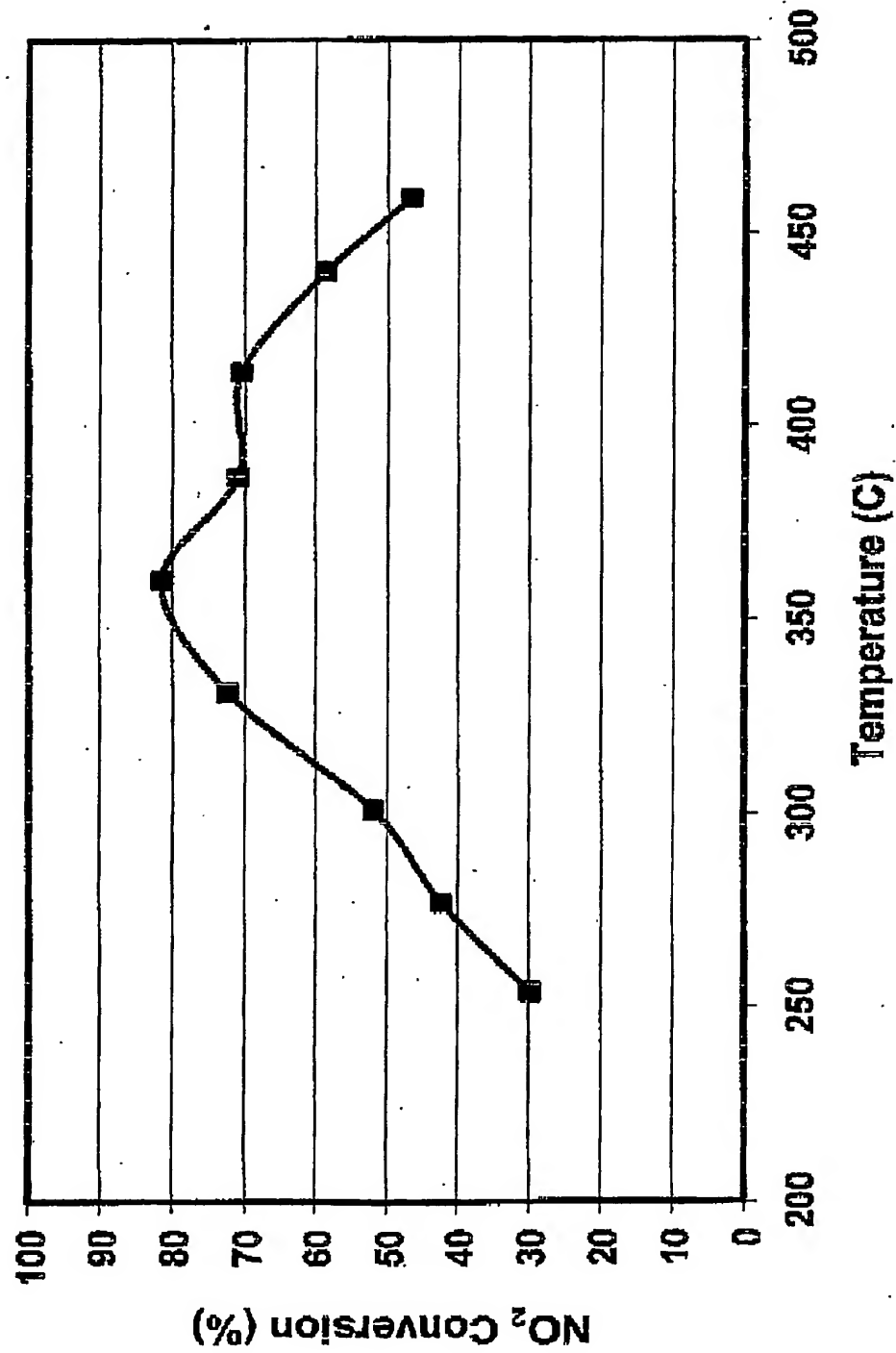


FIG 7.

80 / 08

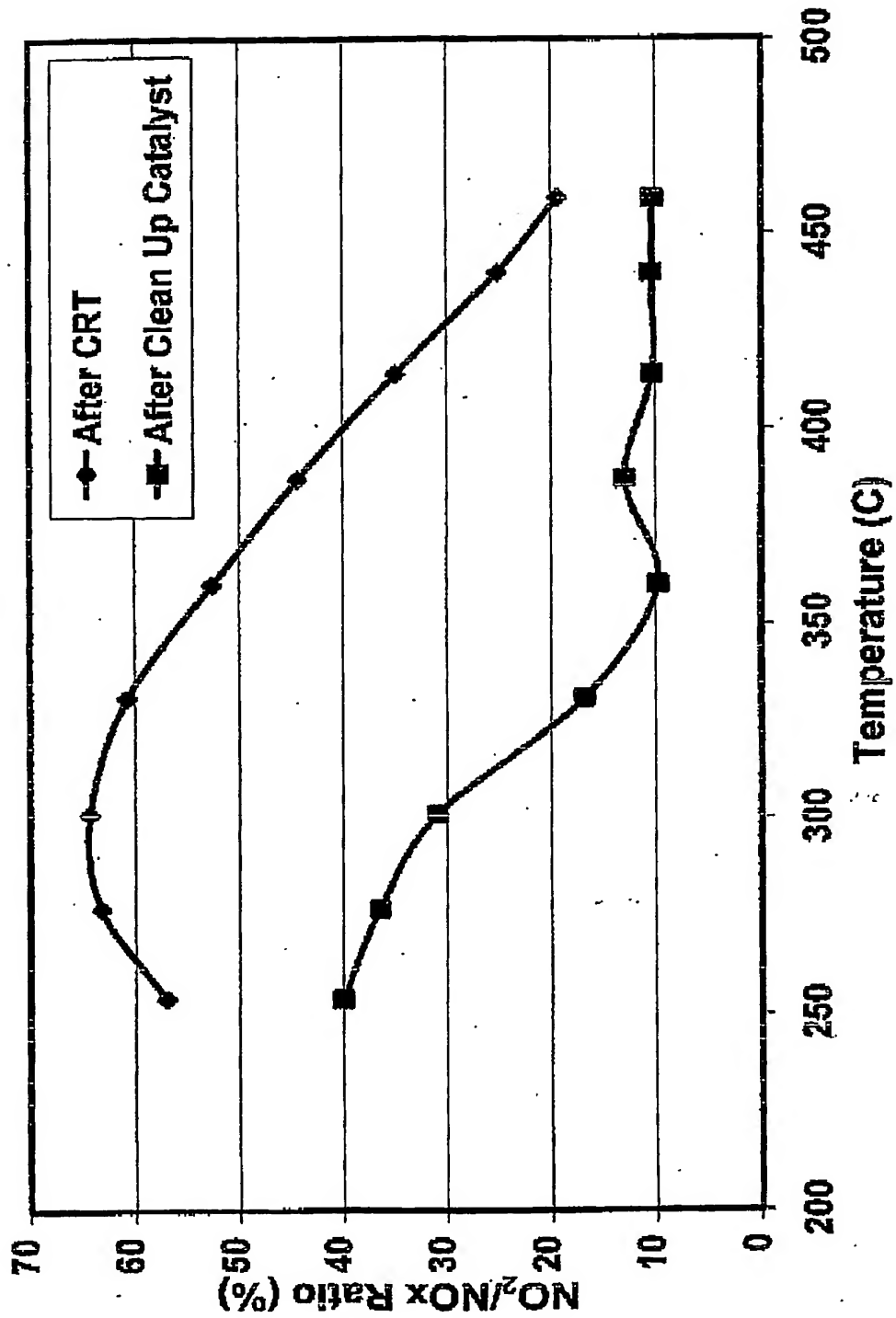


Fig 8.



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**